

Tuning the charge-transfer energy in hole-doped cuprates

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Chemical substitution, combined with strain, allows the charge-transfer energy in hole-doped cuprates to be broadly tuned. We theoretically characterize the structural and electronic properties of the family of compounds $R_2\text{CuO}_2\text{S}_2$, constructed by sulfur replacement of the apical oxygens and rare earth substitutions in the parent cuprate La_2CuO_4 . Additionally, the enthalpies of formation for possible synthesis pathways are determined.

In weakly correlated systems, analytic and computational tools, such as density functional theory (DFT), have achieved a level of control where one can reasonably contemplate materials design. For recent work in this upcoming field, see Refs. [1–5]. The corresponding methods for strongly-correlated systems are rapidly advancing [6–11]. Materials design of correlated systems is a valuable route to test our physical understanding, and should the materials be synthesized, provides experimental feedback to accelerate development of theoretical methods.

The high-temperature cuprate superconductors are classic strongly-correlated systems which exhibit the highest transition temperatures known. Despite intense theoretical and experimental study, we have limited first-principles understanding of the chemical parameters controlling these transition temperatures. Based on an *ab initio* study of the cuprates [12], we proposed that the charge-transfer energy $\epsilon_d - \epsilon_p$ controls the strength of correlations [13] and therefore tunes the maximum superconducting transition temperature $T_{c,\text{max}}$. Starting with the most correlated cuprate La_2CuO_4 , reducing $\epsilon_d - \epsilon_p$ enhances $T_{c,\text{max}}$. In contrast, Sakakibara, *et. al.*, proposed that reducing the admixture of the Cu $3d_{z^2}$ orbital with the in-plane $3d_{x^2-y^2}$ orbital enhances $T_{c,\text{max}}$, a mechanism dubbed “orbital distillation” [14, 15]. These studies pose a challenge for materials design to test the theoretical proposals.

In this work, we design a family of copper oxysulfides to tune the charge-transfer energy of La_2CuO_4 (LCO) and test the proposed theories. We show that substitution of the apical oxygens by sulfur produces sufficiently large effects on $\epsilon_d - \epsilon_p$ and orbital distillation to warrant investigation. The compounds are valuable for differentiating the two theories since, barring competing orders, the proposed mechanisms predict opposite shifts in $T_{c,\text{max}}$ in the oxysulfides relative to the LCO baseline. However, checks on structural stability and the thermodynamics of synthesis pathways indicate epitaxial stabilization is likely necessary for realization of the oxysulfides.

We choose the *T*-type layered perovskite La_2CuO_4 (LCO) as our structural starting point. This single-

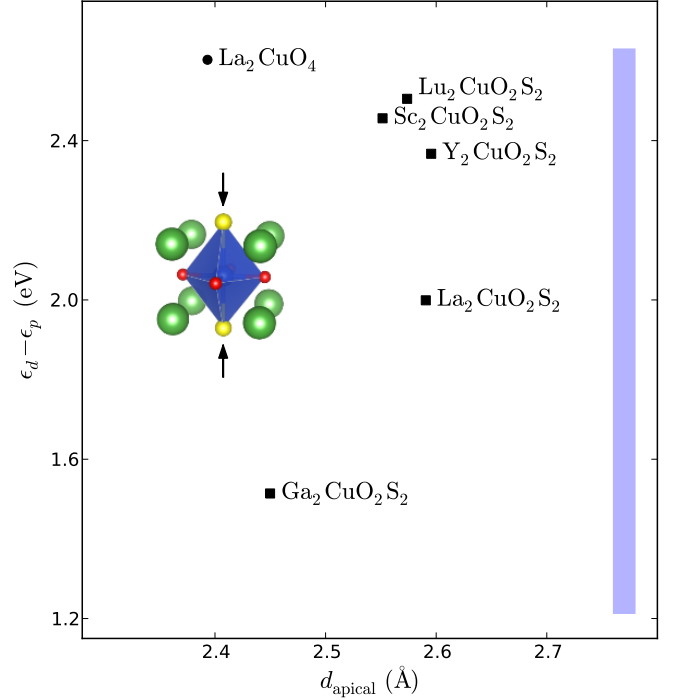


FIG. 1. Scatter plot of the charge-transfer energy ($\epsilon_d - \epsilon_p$) and the apical atom distance from the CuO_2 plane (d_{apical}) for the family of hypothetical copper oxysulfides $R_2\text{CuO}_2\text{S}_2$ (squares) and the actual compound La_2CuO_4 (circle). The oxysulfides are formed by the substitution of apical oxygens by sulfur (arrows in inset figure of crystal structure), and the structure obtained by full relaxation in DFT. Chemical substitution allows us to span nearly the entire range of charge-transfer energies (shaded bar) found in the cuprates.

layered cuprate is well-studied, supports a broad range of doping, and exhibits the largest charge-transfer energy of all the hole-doped cuprates. Guided by the intuition that larger, more covalent, apical ions would decrease $\epsilon_d - \epsilon_p$, we replace the apical oxygens in LCO with sulfur to form the copper oxysulfide $\text{La}_2\text{CuO}_2\text{S}_2$. Due to the larger ionic radii of sulfur relative to oxygen, we expect the LaS charge reservoir layers to be crowded. To compensate for this large sulfur in the charge reservoir layers,

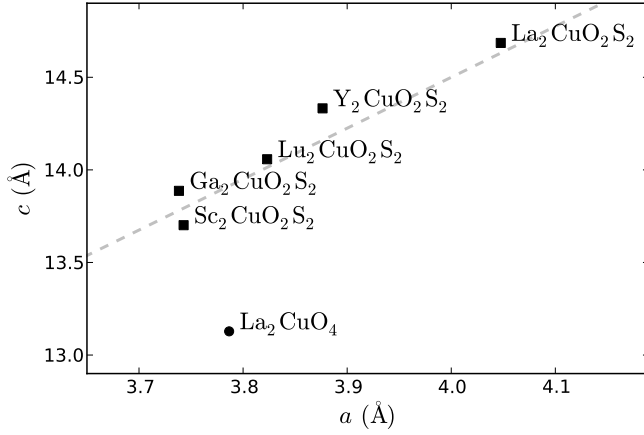


FIG. 2. Fully relaxed conventional cell lattice parameters for $R_2\text{CuO}_2\text{S}_2$ family of compounds (squares) as compared to La_2CuO_4 (dot). Sulfur substitution increases both the a and c lattice parameters. The decrease in the cation's ionic radii from ($\text{La} \rightarrow \text{Y} \rightarrow \text{Lu} \rightarrow \text{Sc} \rightarrow \text{Ga}$) accounts for the contraction of a and c within the family of oxysulfides. The dotted line is a guide to the eye.

we explore the effect substitution of the large La ion with smaller trivalent ions $R = \text{Y}, \text{Lu}, \text{Sc}, \text{Ga}$. We structurally relax, within a single unit cell, the entire family of copper oxysulfides $R_2\text{CuO}_2\text{S}_2$, using the Vinet equation of state [16]. We used the VASP [17–19] density functional software package with PAW potentials [20, 21]. Finally, we extract $\epsilon_d - \epsilon_p$ by performing a full-potential calculation on the relaxed structure using Wien2K [22], then downfolding [23] to orbitals constructed in the manner described in Ref. [24].

The charge-transfer energies for the parent compound La_2CuO_4 and the family of hypothetical oxysulfides $R_2\text{CuO}_2\text{S}_2$ are shown in Fig. 1. The substitution of sulfur alone, leaving the La ion unmodified, decreases the charge-transfer energy by 0.6 eV, a significant reduction given that $\epsilon_d - \epsilon_p$ spans a range of 1.4 eV across all cuprate families. If no competing electronic or structural orders are introduced, we predict $\text{La}_2\text{CuO}_2\text{S}_2$ to have a higher superconducting transition temperature than LCO (which has a $T_{c,\text{max}}$ of 38 K). Further substitution of La by trivalent cations of varying ionic radii allows us to span nearly the entire range of charge-transfer energies found in the cuprates. We find that the apical atom distance d_{apical} is increased by as much as 0.2 Å in the oxysulfides, due to the large size of sulfur.

The structural effects of the sulfur and rare-earth substitutions can be rationalized entirely due to trends in ionic radii, as shown via a scatter plot of the a - and c -axis lattice constants of the proposed compounds (Fig. 2). The ionic radius of sulfur is greater than that of oxygen by 0.4 Å, a significant amount. Apical sulfur substitution alone enhances the c -axis length by over 1.5 Å relative to the parent compound LCO, in agreement with the

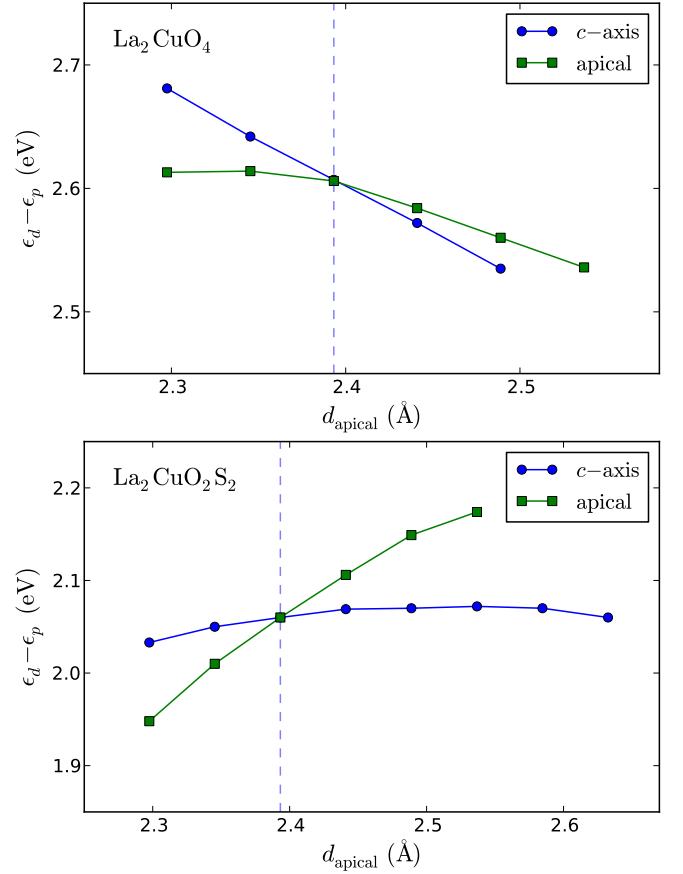


FIG. 3. The effect of uniaxial c -axis strain on the charge-transfer energy (circles) for the actual compound La_2CuO_4 (top) and the oxysulfide $\text{La}_2\text{CuO}_2\text{S}_2$. The dotted line shows the equilibrium d_{apical} . In LCO, uniaxial compression increases $\epsilon_d - \epsilon_p$ and consequently suppresses T_c , as observed experimentally [25], while we predict pressure should hardly affect T_c in the oxysulfide. To disentangle crystal fields from the Madelung potential, we show the effect of tweaking d_{apical} with all other atoms fixed (squares). The effects due to the Madelung potential, roughly quantified by the difference between the two curves, is the same order of magnitude as crystal fields.

fact that there are four sulfur layers in the conventional cell, giving $\Delta c \approx 4 \times 0.4$ Å. This chemically induced strain may be beneficial for superconductivity since it is known uniaxial compression strongly suppresses T_c in La_2CuO_4 [25], a point we will subsequently address. In contrast, the in-plane constant exhibits only a slight expansion by 0.2 Å, due to the restraining effect of the stiff Cu-O bonds. The subsequent rare-earth substitutions in the oxysulfides drive a clear structural trend, with both lattice parameters contracting in parallel with the decreasing ionic radius of the rare-earth ion R . The same trend is experimentally observed in the T' -type $R_2\text{CuO}_4$ family [26].

In order to disentangle the structural contributions driving variations in the charge-transfer energy, we track

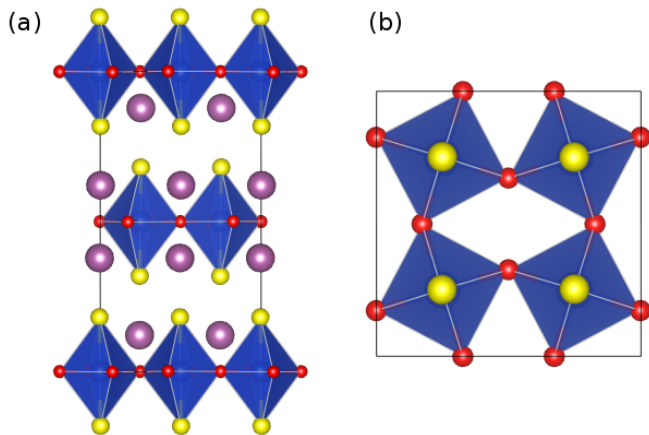


FIG. 4. Octahedral rotations in $\text{Sc}_2\text{CuO}_2\text{S}_2$ as shown by (a) a view along the a -axis, and (b) a section of the CuO_2 plane. We structurally relaxed a $2 \times 2 \times 1$ supercell with no symmetry constraints. While there is no out-of-plane buckling of the Cu-O bonds, the small Sc ion causes strong in-plane rotations of the octahedral cages (denoted $a^0a^0c_p^-$ in Glazer notation). The compound remains in the tetragonal T -type phase.

the change in $\epsilon_d - \epsilon_p$ as we (1) vary the c -axis parameter, modeling uniform uniaxial strain and (2) vary d_{apical} alone with all other atomic positions fixed. The difference in the resultant $\epsilon_d - \epsilon_p$ between these two structural configurations provides a rough proxy for the magnitude of effects due to the Madelung potential as compared to the local crystal fields generated in part by the apical atom. For the parent compound LCO (Fig. 3 top), c -axis compression enhances $\epsilon_d - \epsilon_p$. This increase in correlation strength provides a natural explanation for the observed suppression of superconductivity with uniaxial pressure [25]. Modifying d_{apical} alone has a similar, albeit smaller, effect. The difference between the two curves is of the same magnitude as the total shifts in $\epsilon_d - \epsilon_p$, so we conclude that crystal fields and Madelung potentials have similar energy scales, making first-principles calculations necessary for quantitative insight. In comparison, strain has the opposite effect in the hypothetical compound $\text{La}_2\text{CuO}_2\text{S}_2$ (Fig. 3 bottom), with c -axis compression driving a reduction in $\epsilon_d - \epsilon_p$. Thus, $T_{c,\text{max}}$ should be observed to trend in the opposite direction as compared to the parent compound.

Finally, we check the structural and thermodynamic stability of the hypothetical oxysulfides. Determining the lowest-energy structure of a general multi-element compound is extremely challenging, and the checks we perform are by no means exhaustive. However, guided by knowledge of typical competing phases and structural distortions, we show the $R_2\text{CuO}_2\text{S}_2$ family passes several basic criteria for stability.

In La_2CuO_4 , when the large La ion is replaced by the smaller Nd and Pr atoms, the oxygens in the rock-salt LaO layers in the T -type structure tend to be unstable

ΔE	ΔV	Synthesis pathway
141	-7.3	$\text{La}_2\text{O}_2\text{S} + \text{CuS} \rightarrow \text{La}_2\text{CuO}_2\text{S}_2$
223	-3.4	$\text{Y}_2\text{O}_2\text{S} + \text{CuS} \rightarrow \text{Y}_2\text{CuO}_2\text{S}_2$
267	-5.0	$\text{Lu}_2\text{O}_2\text{S} + \text{CuS} \rightarrow \text{Lu}_2\text{CuO}_2\text{S}_2$
356	-3.0	$\text{Sc}_2\text{O}_2\text{S} + \text{CuS} \rightarrow \text{Sc}_2\text{CuO}_2\text{S}_2$
101	-4.9	$\text{La}_2\text{O}_2\text{S}_2 + \text{Cu} \rightarrow \text{La}_2\text{CuO}_2\text{S}_2$
148	-3.3	$\text{La}_2\text{O}_3 + \text{CuS} \rightarrow \text{La}_2\text{CuO}_3\text{S}$
454	-0.7	$\text{Sc}_2\text{O}_3 + \text{CuS} \rightarrow \text{Sc}_2\text{CuO}_3\text{S}$
97	-4.9	$\text{La}_2\text{O}_2\text{S} + \text{CuO} \rightarrow \text{La}_2\text{CuO}_3\text{S}$
269	2.8	$\text{Sc}_2\text{O}_2\text{S} + \text{CuO} \rightarrow \text{Sc}_2\text{CuO}_3\text{S}$
28	-5.1	$\text{La}_2\text{O}_3 + \text{CuO} \rightarrow \text{La}_2\text{CuO}_4$

TABLE I. Synthesis pathways for various cuprate oxysulfides based on substitution of sulfur for both (top block) or only one (middle block) of the apical oxygens in $R_2\text{CuO}_4$. Energies in kJ/mol and volumes in kJ/mol/GPa. Since the energies of formation ($\Delta E = E_{\text{products}} - E_{\text{reactants}}$) are positive, none of these pathways appear favorable at ambient conditions. However, high-pressure synthesis will help stabilize these pathways, since the majority of volume differentials ($\Delta V = V_{\text{products}} - V_{\text{reactants}}$) are negative. We benchmark our method against the standard synthesis pathway for La_2CuO_4 , shown on the last line. Surprisingly, ΔE is +28 kJ/mol, so either DFT systematically overestimates enthalpies (which means the actual enthalpies for our hypothetical compounds are *smaller*, in our favor), or we must add a bi-directional uncertainty of ± 30 kJ/mol to the computed enthalpies. Additionally, positional entropy of the apical S in the half-substituted $R_2\text{CuO}_3\text{S}$ compounds should also assist in synthesis.

towards rearrangement into the fluorite structure, forming the T' -type structure associated with the electron-doped cuprates [27]. We check whether our T -type oxysulfides are locally stable against distortion into the T' -type structure by performing a full structural relaxation in a $2 \times 2 \times 1$ supercell with no symmetry constraints. We choose $\text{Sc}_2\text{CuO}_2\text{S}_2$ as a representative compound, since we believe that the smaller Sc cation will help create room for the large sulfur anion. The resultant structure (Fig. 4) shows strong octahedral rotations along the c -axis, denoted $a^0a^0c_p^-$ in Glazer notation [28]. Perovskite structures often exhibit octahedral rotations when the Goldschmidt tolerance factor $t = (r_A + r_O)/\sqrt{2}(r_B + r_O)$ is less than unity as the octahedra rotate to fill the empty space left by substitution of small rare-earth ions. However, we find the T -type structure to be locally stable and expect the rotations to be smaller in magnitude for the larger $R = \text{La}$ ion. Additionally, the system remains tetragonal and shows no out-of-plane buckling of the Cu-O bonds known to be detrimental to superconductivity [29]. We note that recent advances have allowed experimental control over the two competing structures in compound synthesis [26], which will help overcome these structural hurdles.

In addition to local structural stability, we check the

thermodynamic stability of the proposed compounds with respect to competing phases. We assemble the computed internal energies of formation $\Delta E = E_{\text{products}} - E_{\text{reactants}}$ in Table I (units of kJ/mol). That the quantities are positive imply the that these standard pathways are not energetically favorable at zero pressure. However, it is known that many functional materials are metastable, protected from decay by large energetic barriers, resulting in technologically useful lifetimes [2]. Typical energetic deficits range from 5 to 30 kJ/mol, when translated to the oxysulfide compound stoichiometries. Accompanied by the fact that the volume differentials $\Delta V = V_{\text{products}} - V_{\text{reactants}}$ are negative, high pressure synthesis may allow the products to form. Furthermore, we included in Table I compounds of the form $R_2\text{CuO}_3\text{S}$, where only half of the apical oxygens are replaced by sulfur. The configurational entropy of the sulfur-oxygen arrangement in the charge-reservoir blocks will further encourage product formation. These challenges in stability suggest the oxysulfides could be an ideal system for other materials synthesis techniques like molecular beam epitaxy.

Turning to the orbital distillation theory, we show in Fig. 5 the effect of sulfur substitution on the energy splitting $\Delta E = \epsilon_{x^2-y^2} - \epsilon_{z^2}$, which quantifies the strength of the $3d_{z^2}$ admixture into the $3d_{x^2-y^2}$ band. We find that apical sulfurs, being a larger, more covalent ion than oxygen, generally decreases ΔE , causing stronger mixing of the d_{z^2} orbital into the $d_{x^2-y^2}$ band, which suppresses $T_{c,\text{max}}$ in the two-orbital model. Barring competing orders, the two proposals predict diverging effects: the reduction of $\epsilon_d - \epsilon_p$ should enhance $T_{c,\text{max}}$ in the oxysulfides, while the increase mixing of d_{z^2} suppress $T_{c,\text{max}}$.

In conclusion, we have designed via first-principles a family of copper oxysulfides, based on the well-studied cuprate La_2CuO_4 , which offer broad tunability in the charge-transfer energy. According to our proposal, the replacement of oxygen by sulfur in the apical position will enhance the superconducting $T_{c,\text{max}}$, while the orbital distillation proposal predicts the opposite effect. Although we recognize that many other mechanisms can drive changes in transition temperatures, we nevertheless believe that exploration of the oxysulfides are a valuable step towards testing the proposed theories. We find that molecular beam epitaxy is the preferred synthesis route since epitaxy will reduce competing orders and tip the energetics away from competing phases. Natural extensions of this work include generating a detailed *ab initio* understanding of the structural handles controlling electronic parameters and pursuing similar chemical engineering of crystal field levels in the Bi, Tl and Hg-based cuprate families.

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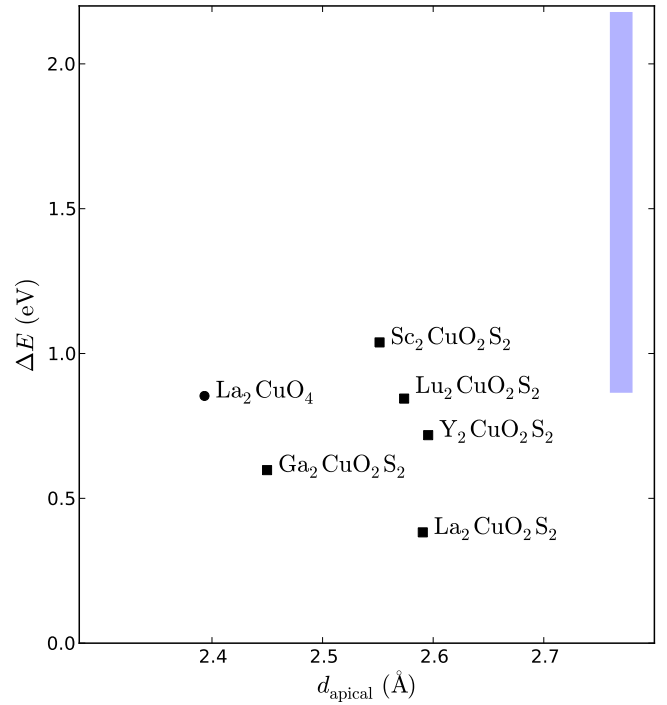


FIG. 5. The energy splitting $\Delta E = E_{x^2-y^2} - E_{z^2}$ between the onsite energies of the $d_{x^2-y^2}$ and d_{z^2} orbitals among the copper oxysulfide family (squares). For comparison is the actual compound La_2CuO_4 (circle). The physical range of ΔE spanned by the single-layer cuprates is shown with a shaded bar (from Sakakibara, *et. al.*) [15]. The ΔE in the oxysulfides are generally smaller, implying stronger mixing of the d_{z^2} orbital with the in-plane $d_{x^2-y^2}$ orbital. Thus, barring other competing orders, sulfur substitution should enhance $T_{c,\text{max}}$ according to the charge-transfer theory, while $T_{c,\text{max}}$ will be suppressed according to the two-orbital theory.

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